Stabilization of long-wavelength modes on the interface in electrodeposition

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A model is proposed for electrochemical deposition that can describe the flat, dense pattern constituting an assembly of needles with a flat envelope. The model is represented by a pair of diffusion equations that govern mass transport in the electrostatic field. A linear-stability theory is applied to investigate whether or not the interface of the aggregate is stable, following Saffman and Taylor [Proc. R. Soc. London, Ser. A **245**, 312 (1958)]. It is found that the disturbances with a wavelength longer than a critical wavelength become stable on the interface of the aggregate. When the destabilizing force of the Saffman-Taylor instability becomes smaller than the stabilizing force of the electrostatic field at the long-wavelength modes, then the flat, dense pattern occurs.

I. INTRODUCTION

Pattern formation in systems far from equilibrium is a subject of considerable current interest.¹⁻¹¹ A number of models for cluster formation have been proposed, and a variety of computer simulations have been carried out to investigate the relations between the cluster geometry and growth mechanisms. The structure of the aggregates strongly depends on the dynamics of the growth process. Examples of pattern formation in diffusive systems include crystal growth,¹²⁻¹⁸ electrochemical deposition,¹⁹⁻²³ viscous fingering,²⁴⁻²⁶ and dielectric breakdown.²⁷ Witten and Sander²⁸ proposed the diffusion-limited aggregation (DLA) model to treat the pattern formation in the diffusive field. The structure of the aggregate has been analyzed by computational,^{28,29} experimental,^{19,20,24,25} and analytical methods.³⁰⁻³² It has been found that the structure of the aggregate was a fractal. Several approaches to simple generalizations of the DLA model have been carried out to take into account surface tension,³³⁻³⁵ particle drift,³⁶⁻³⁸ multiparticle effects,^{39,40} sticking probability,^{39,41} and lifetime effects.⁴² The crossover phenomena from the DLA fractal to the nonfractal structure were found. Recently, Grier *et al.*²⁰ and Sawada *et al.*²¹ found in experiments of the electrochemical deposition that the system was driven from fractal growth, through dense radial aggregation, to dendritic growth by varying the applied potential and the concentration of the electrolyte. Hibbert and Melrose²³ carried out the electrodeposition experiment on paper to prevent convective motion. They found only the crossover to the dense radial aggregation by increasing the applied voltage. Nagatani⁴³ proposed a model to take into account the effect of growing interface on the DLA fractal. By using a biased random walker governed by the Laplace equation, the crossovers from the DLA fractal to the flat dense aggregation and to the needlelike structure were found, depending upon the sign of the convective term. The question of whether or not the crossover to the flat, dense aggregation occurs without convective motion suggested by Hibbert and Melrose,²³ is an attractive subject.

Halsey⁴⁴ presented a model to take into account the double layer at the metallic surface. He found a weak morphological instability. Grier *et al.*⁴⁵ proposed a model in which stability arose from the resistivity of the growth channels.

In this paper, we propose a model to describe the crossover from the DLA fractal to the flat, dense aggregation. The model is represented by a pair of diffusion equations that govern mass transport in the electrostatic field. Following Saffman and Taylor,⁴⁶ we apply the linear-stability theory to the problem of the interface in the electrodeposition. We study the subject of whether or not the envelope of the interface becomes flat. We find the stabilization mechanism of the interface on a wavelength longer than a critical value. When the destabilizing force of the Saffman-Taylor instability becomes smaller than the stabilizing force of the electrostatic field at long-wavelength modes, then the flat and dense pattern appears. In the limit of zero mobilities of ions, the mass transport decouples with the electric field. Then, our analysis precisely describes the Saffman-Taylor instability.

The organization of the paper is as follows. In Sec. II we present the basic equations of mass transport in an electric field. Our model is given by a pair of the diffusion equations: the mass transport equation and the electrostatic potential equation. In Sec. III we apply the Saffman-Taylor approach to the stability problem of the interface in the electrochemical deposition. The stabilization of the interface is found at a wavelength longer than a critical value. In Sec. IV we present the simulation result. The morphology is found to consist of an assembly of needles with a flat envelope. In Sec. V we present the summary.

II. BASIC EQUATION AND MODEL

In the absence of convective motion, ions in the solution flow in response to an applied electric field and a concentration gradient. The currents of the positive and negative ions are thus written as

$$J_{+,i} = -z_+\mu_+C_+ \frac{\partial\Phi}{\partial x_i} - D_+ \frac{\partial C_+}{\partial x_i}, \quad (1)$$

$$J_{-,i} = -z_-\mu_-C_- \frac{\partial\Phi}{\partial x_i} - D_- \frac{\partial C_-}{\partial x_i}, \quad (2)$$

where the D 's, μ 's, z 's, and C 's are, respectively, the diffusion constants, mobilities, charges, and concentrations of the different ions. The concentrations satisfy the mass-transport equations in the electric field under the quasistationary approximation

$$\frac{\partial J_{+,i}}{\partial x_i} = 0, \quad (3)$$

$$\frac{\partial J_{-,i}}{\partial x_i} = 0, \quad (4)$$

with

$$\frac{\partial^2 \Phi}{\partial x_i^2} = 0. \quad (5)$$

We consider disturbances of the concentration and electric fields induced by small deviations of the interface. The concentration and electric fields are separated into the undisturbed and disturbed parts

$$C = \langle C \rangle + \tilde{C}, \quad (6)$$

$$\Phi = \langle \Phi \rangle + \tilde{\Phi}. \quad (7)$$

For the undisturbed part, the current is completed by the dissolution of the anode and the electroneutrality in the solution holds:

$$\langle J_{-,i} \rangle = 0, \quad (8)$$

$$z_+ \langle C_+ \rangle + z_- \langle C_- \rangle = 0. \quad (9)$$

Thus, we obtain

$$z_+\mu_+ \langle C_+ \rangle \frac{\partial \langle \Phi \rangle}{\partial x_i} = -(z_+\mu_+/z_-\mu_-)D_- \frac{\partial \langle C_+ \rangle}{\partial x_i}. \quad (10)$$

Here we assume

$$z_+\mu_+C_+ \frac{\partial \langle \Phi \rangle}{\partial x_i} = -(z_+\mu_+/z_-\mu_-)D_- \frac{\partial C_+}{\partial x_i}. \quad (11)$$

From Eqs. (1), (3), (5), and (11), the transport equation of the positive ion is given by

$$\frac{\partial}{\partial x_i} \left[z\mu C \frac{\partial \tilde{\Phi}}{\partial x_i} + D \frac{\partial C}{\partial x_i} \right] = 0, \quad (12)$$

$$\nabla^2 \tilde{\Phi} = 0, \quad (13)$$

where $z\mu = z_+\mu_+$ and $D = D_+ - (z_+\mu_+/z_-\mu_-)D_-$.

Equations (12) and (13) are the basic equations for the mass transport of a positive ion in the electric field. The mass transport by the undisturbed electric field is included as the effective diffusion. The disturbed electric field

induced by a small deviation of interface contributes to the electrical migration.

III. LINEAR-STABILITY THEORY

We consider the problem of whether or not the flat interface is stable in two dimensions when the aggregate is forming in the diffusion field within the electrostatic field [see Fig. 1(a)]. We apply the Saffman-Taylor approach to the stability problem of the flat interface. Our basic equations are given by Eqs. (12) and (13). To describe a disturbance of the concentration induced by small deviations of the interface, separate the concentration field into the undisturbed and disturbed parts, the instantaneous position of the undisturbed interface coinciding with the plane $x=0$. Suppose that the flat interface is deformed slightly into a wavelike corrugation of wave number m described by

$$x = \delta(t) \cos(my). \quad (14)$$

The undisturbed part of concentration is given by

$$\nabla^2 \langle C \rangle = 0, \quad (15)$$

$$\langle C \rangle = C_s, \quad x=0, \quad (16)$$

$$\langle C \rangle = C_\infty, \quad x=L. \quad (17)$$

The solution of the unperturbed part is given by

(a)

(b)

FIG. 1. (a) Schematic representation of the diffusive system within the electric field. To describe a disturbance of the flat interface, take rectangular coordinates (x,y) , the instantaneous position of the undisturbed interface coinciding with the plane $x=0$. (b) The model used to simulate the diffusion process in the electric field. A voltage is applied between the upper and the lower boundaries to induce a periodic boundary condition (BC). A single particle is introduced at a time at a randomly chosen point on the upper boundary, and a biased random walk where a bias varies from position to position is performed, and is given by Eq. (35).

$$\langle C \rangle = C_s + (\Delta C/L)x, \quad (18)$$

where $\Delta C = C_\infty - C_s$. The disturbed part of concentration is governed by

$$\frac{\partial}{\partial x_i} \left[z\mu \langle C \rangle \frac{\partial \tilde{\Phi}}{\partial x_i} + D \frac{\partial \tilde{C}}{\partial x_i} \right] = 0, \quad (19)$$

$$z\mu C_s \frac{\partial \tilde{\Phi}}{\partial x} + D \frac{\partial \tilde{C}}{\partial x} = C_a \dot{x}, \quad x=0 \quad (20)$$

$$\tilde{C}=0, \quad x=L, \quad (21)$$

where the boundary condition (20) is given by the mass conservation law on the interface and C_a is the concentration of the aggregate. The disturbed part of electrostatic field is governed by

$$\nabla^2 \tilde{\Phi} = 0, \quad (22)$$

$$(\sigma_s/z) \frac{\partial \tilde{\Phi}}{\partial x} = C_a \dot{x}, \quad x=0 \quad (23)$$

$$\tilde{\Phi}=0, \quad x=L \quad (24)$$

where σ_s is the conductivity in the solution. The boundary condition (23) is obtained from the condition that the current on the interface is proportional to the mass flux. The solution of the perturbed part (22) is given by

$$\tilde{\Phi} = -(C_a z / \sigma_s) (\delta/m) \cos(my) e^{-mx}, \quad (25)$$

where the system size L is sufficiently large.

Inserting Eq. (25) into Eq. (19), we obtain the solution of the perturbed part (19)

$$\begin{aligned} \tilde{C} = & -A (\delta/m) \cos(my) e^{-mx} \\ & + (x/2m) (\Delta C/DL) (z^2 \mu C_a / \sigma_s) \delta \cos(my) e^{-mx}. \end{aligned} \quad (26)$$

Here the unknown constant A is determined by the boundary condition (20):

$$A = C_a/D - (1/2m) (\Delta C/DL) (z^2 \mu C_a / \sigma_s), \quad (27)$$

where we assume $C_s \approx 0$.

Adding Eq. (26) to Eq. (18) and taking into account to the first order of δ , set $x=0$. We obtain the governing equation of the amplitude of the deformed interface:

$$\dot{\delta} = (m/A) (\Delta C/L) \delta. \quad (28)$$

In the limit of a sufficiently small mobility, Eq. (28) reduces to a variant of the Saffman-Taylor instability: $\dot{\delta} = m(D\Delta C/LC_a)\delta$. By replacing $(D\Delta C/LC_a)$ with the velocity v , Eq. (28) precisely reproduces the Saffman-Taylor instability: $\dot{\delta} = mv\delta$. Our result is an extended version of the Saffman-Taylor instability.

Since the total mass flow is proportional to the total current, we obtain

$$\Delta C = (\sigma_s/z) D^{-1} \Delta \Phi, \quad (29)$$

where $\Delta \Phi$ is the applied voltage. Using Eq. (29), we obtain from Eq. (27)

$$A = (C_a/D) [1 - (2mL)^{-1} (z\mu/D) \Delta \Phi]. \quad (30)$$

Here we define the critical wave number m_c as $A=0$:

$$m_c = (2L)^{-1} (z\mu/D) \Delta \Phi. \quad (31)$$

If $m < m_c$, then $A < 0$. A disturbance with wave number m smaller than the critical wave number m_c becomes stable. If $m > m_c$, then $A > 0$. A disturbance with wave number m larger than the critical wave number m_c becomes unstable. Thus the interface is stabilized at long length scales. We find a stabilizing mechanism of the interface on the long-wavelength modes. By the mechanism in which the interface is stable at long length scales and unstable at short length scales, the flat, dense pattern which consists of an ensemble of needles appears. The distance between the nearest-neighbor needles is approximately given by the critical wavelength. The distance becomes shorter with increasing applied voltage. These results will have bearing upon the dense radial patterns which have been seen recently in some two-dimensional electrodeposition experiments. We shall perform the simulation of our model to make the flat, dense pattern in the following section.

IV. SIMULATION OF FLAT, DENSE PATTERN

We construct the simulation model to describe the pattern forming in the electrodeposition. We cast the basic equations in dimensionless form. We use the following units: the concentration difference $\Delta C (= C_\infty - C_a)$ for the concentration, the applied voltage $\Delta \Phi$ for the electrostatic potential, and L for distance. Then Eq. (12) becomes

$$\frac{\partial}{\partial \hat{x}_i} \left[\chi \hat{C} \left(\frac{\partial \hat{\Phi}}{\partial \hat{x}_i} - \left\langle \frac{\partial \hat{\Phi}}{\partial \hat{x}_i} \right\rangle \right) + \frac{\partial \hat{C}}{\partial \hat{x}_i} \right] = 0, \quad (32)$$

with

$$\nabla^2 \hat{\Phi} = 0, \quad (33)$$

where $\chi = (z\mu/D) \Delta \Phi$ and $\hat{C} = (C - C_a)/\Delta C$. Cared variables are all dimensionless. We find the important dimensionless parameter χ representing the strength of the electrical migration to the diffusion. Now we consider the simulation of the aggregation process following Eqs. (32) and (33). The diffusing particles undergo random walks except for a bias resulting from the electrical migration. We simulate the aggregation process by using the biased random walkers. The bias varies from position to position. The local strength of the bias is calculated step by step by the Laplace equation under the boundary conditions of the instantaneous aggregate. The biased random walker continues to move until it arrives at the surface of the aggregate. The probability that the biased random walker visits the site (i, j) satisfies the equation

$$\begin{aligned} p(i, j) = & \left(\frac{1}{4} + \alpha_x \right) p(i+1, j) + \left(\frac{1}{4} - \alpha_x \right) p(i-1, j) \\ & + \left(\frac{1}{4} + \alpha_y \right) p(i, j+1) + \left(\frac{1}{4} - \alpha_y \right) p(i, j-1), \end{aligned} \quad (34)$$

with

FIG. 2. Typical patterns grown with use of the model described by Eqs. (32) and (33). (a) Aggregate of 636 particles for $\chi=16$. (b) Aggregate of 916 particles for $\chi=32$. (c) Aggregate of 1040 particles for $\chi=48$. (d) Aggregate of 1080 particles for $\chi=64$. (e) Aggregate of 1191 particles for $\chi=80$. With increasing χ , the flat, dense pattern appears to consist of an assembly of needles with a flat envelope.

$$\alpha_x = \chi [\hat{\Phi}(i+1, j) - \hat{\Phi}(i-1, j) - \langle \hat{\Phi}(i+1, j) - \hat{\Phi}(i-1, j) \rangle_s] / 8, \quad (35)$$

$$\alpha_y = \chi [\hat{\Phi}(i, j+1) - \hat{\Phi}(i, j-1)] / 8,$$

where $\hat{\Phi}$ is obtained by solving the Laplace equation under the boundary conditions of the instantaneous aggre-

FIG. 3. The plot of the surface thickness vs χ .

gate, and $\langle \rangle_s$ indicates the average value of the electric field over the interface. Equations (34) and (35) were previously derived to study the effect of growing interface on the DLA. In a previous paper,⁴³ we investigated the convection effect induced by the growing interface. The bias resulted from the growing interface. In this case, the bias results from the electrical migration. The simulation procedure is similar to the previous paper⁴³ except for the system size. In this case, the control parameter χ is always a positive value, in contrast to the growing interface effect.

We summarize the algorithm of the simulation process [see Fig. 1(b)]. We start by setting the potentials $\hat{\Phi}=0$ and 1 on the aggregate and the upper boundary. We solve the Laplace equation under the boundary conditions. We evaluate the local bias from Eq. (35). Particles are introduced one at a time at a randomly chosen point on the upper boundary. The particle performs a biased random walk following Eq. (34). The particle continues to move until it either reaches a point adjacent to a site already occupied by a particle or until it reaches the upper boundary. If the particle sticks on the aggregate, we solve the Laplace equation under the boundary conditions with the configuration of the aggregate. We repeat the procedure.

We have carried out calculations for a range of $\chi [(z\mu/D)\Delta\Phi]$ values, on square arrays of size 80×80 . The clusters are grown until the height reaches 40 units. The patterns formed in the diffusive system are shown in Fig. 2 for a number of χ . Figures 2(a)–2(e) show, respectively, the aggregates for $\chi=16, 32, 48, 64$ and 80 . The aggregates consist of 636, 916, 1040, 1080, and 1191 particles, respectively, for Figs. 2(a)–2(e). With increasing χ the interface of the aggregate becomes flat overall. The flat, dense pattern is constructed by an assembly of needles with a flat envelope. For $\chi=0$ the DLA fractal is recovered. We calculate the surface thickness for study-

ing the stabilizing effect of electrical field on the interface. The surface thickness in this case is obtained from

$$\sigma = \left[\sum_i (h_i - \langle h \rangle)^2 \right]^{1/2},$$

where h_i is the height of the deposit at site i , and $\langle h \rangle$ is the mean height. Figure 3 shows the plot of the surface thickness against χ . The surface thickness reduces rapidly with increasing χ . The electrical field stabilizes the interface. The crossover from the DLA fractal to the flat, dense aggregation is found with increasing parameter χ . The distance between nearest-neighbor needles is more shorter with increasing χ . The average number of needles is approximately proportional to χ value. This is consistent with the result (31) obtained from linear-stability theory. Thus we find a stabilizing mechanism of the interface on the long-wavelength modes.

V. SUMMARY

We present a model to describe the flat, dense pattern which consists of an assembly of needles with a flat envelope. The model is governed by a couple of diffusion equations: mass and electrostatic potential. By applying the linear-stability theory to the problem of whether or not the flat interface is stable, we find a stabilization mechanism of the flat interface on long-wavelength modes. The disturbances die out at wavelengths longer than a critical wavelength, but become amplified at shorter wavelengths. The critical wave number is proportional to the applied voltage. The flat, dense aggregate with more needles appears with increasing applied voltage. We carry out the simulation by using the biased random walker. The fat, dense pattern is found to consist of an assemble of needles.

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